

Combining quantum and classical density functional theory for ion-electron mixtures.

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We combine techniques from quantum and from classical density functional theory (DFT) to describe electron-ion mixtures. For homogeneous systems, we show how to calculate ion-ion and ion-electron correlation functions within Chihara's quantum hypernetted chain approximation, which we derive within a DFT formulation. We also sketch out how to apply the DFT formulation to inhomogeneous electron-ion mixtures, and use this to study the electron distribution at the liquid-solid interface of Al. PACS numbers:71.22.+i,61.10.-i,61.20.Gy,61.12.Bt

I. INTRODUCTION

Density functional theory (DFT) has proven itself a remarkably successful tool in condensed matter physics [1]. The foundations were laid in 1964, when Hohenberg and Kohn (HK) [2] proved that the ground state energy of any quantum mechanical system could be described as a functional of the one-body density only. Subsequently, Kohn and Sham [3] developed an orbital based method which could be applied to electronic systems, and Mermin [4] extended the HK proof to finite temperatures, opening up the possibility of using DFT to calculate the free-energy of a statistical mechanical system. Since then many different practical methods have been developed to apply DFT to electronic problems, with countless applications in condensed matter physics, chemistry, and biology [5]. Examples of electronic structure techniques relevant to this paper are the *ab initio* molecular dynamics (AIMD) method of Car and Parrinello [6] and the orbital free *ab initio* molecular dynamics (OF-AIMD) scheme of Madden and co-workers [7]. In a parallel development, the finite temperature version of DFT has been widely used to study classical systems, with myriad applications to phase-transitions and the theory of fluids (in its broadest sense), see e.g. [8,9] for reviews.

However, the classical and quantum versions of DFT have rarely been combined – the two fields have largely developed independently. In this paper we will attempt to bring together these two strands of DFT into one unified formalism, with the aim of applying them to liquid metals. These are ideal systems for which to test a mixed quantum-classical DFT approach since they can be viewed as binary mixtures of classical ions and quantum electrons.

To begin, we first define a two-component free-energy functional

$$F[\rho_I, \rho_e] = F_I^{id}[\rho_I] + F_e^{id}[\rho_e] + F^{ex}[\rho_I, \rho_e], \quad (1)$$

split into the usual way between the ideal free energies of the ions, F_I^{id} , and the electrons, F_e^{id} , and the excess free energy F^{ex} , which is a functional of both one-body densities $\rho_I(\mathbf{r})$ and $\rho_e(\mathbf{r})$. This unique intrinsic free-energy functional obeys the variational principle:

$$\frac{\delta F[\rho_I, \rho_e]}{\delta \rho_\alpha(\mathbf{r})} + \phi_\alpha(\mathbf{r}) = 0, \quad (2)$$

where the $\phi_\alpha(\mathbf{r})$ are the external potentials which uniquely induce the one-body densities $\rho_\alpha(\mathbf{r})$. This principle is subject to the constraint that the integral of $\rho_\alpha(\mathbf{r}) = N_\alpha$, the total number of particles of species $\alpha = \{e, I\}$. We will apply this free-energy functional both to homogeneous and to inhomogeneous liquid metals.

In section II we use the DFT formulation to derive the quantum Ornstein Zernike(QOZ) equations. From these we can derive a set of integral equations, called the quantum hypernetted chain approximation(QHNC) by Chihara [10], which self-consistently solves for the ion-ion and ion-electron pair correlation functions in a homogeneous liquid metal. The great simplification of the QHNC approach is that the original many-centre electronic problem is reduced to an effective one-centre problem, which is much easier to solve. As a specific application, we study the ion-electron radial distribution function for a set of simple metals.

In section III we extend this DFT formulation to inhomogeneous fluids. By using a simple version of this functional, we compare the electron density profile at the liquid-solid interface of Al to the recent simulations using OF-AIMD [11]. We end with some conclusions.

II. APPLYING TWO-COMPONENT DFT TO HOMOGENEOUS LIQUID METALS

A. Quantum Ornstein Zernike equations

DFT provides a nicely unified route to the correlation functions of homogeneous fluids. To begin, we first show how to derive the QOZ relations by defining the direct correlation function as the second functional derivative of the excess free-energy defined in Eq. (1):

$$\frac{1}{\beta} C_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \frac{-\delta^2 F^{ex}}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\beta(\mathbf{r}')} = (\chi_{\alpha\beta})^{-1} - (\chi_{\alpha\beta}^0)^{-1}, \quad (3)$$

where $(\chi_{\alpha\beta})^{-1}$ is the inverse susceptibility matrix of the full system, and $(\chi_{\alpha\beta}^0)^{-1}$ is the inverse susceptibility matrix of the ideal system. These relationships between direct correlation functions and inverse susceptibilities are called the QOZ equations, and they hold for an arbitrary number of components. If any components are classical, then the susceptibilities can be connected to the pair-correlations through the fluctuation-dissipation theorem [12]:

$$\lim_{\hbar \rightarrow 0} \chi_{\alpha\beta}(k, 0) = -\beta(\rho_\alpha^0 \rho_\beta^0)^{1/2} S_{\alpha\beta}(k), \quad (4)$$

where the $S_{\alpha\beta}(k)$ are the structure factors, defined in the usual way [13,14], and we have taken the homogeneous limit and the ρ_α^0 are the homogeneous limits of the densities $\rho_\alpha(\mathbf{r})$. Specializing to the homogeneous limit for two components, with one component being classical (the case at hand), the QOZ equations reduce to a set of relationships between the direct correlation functions and the ion-ion and ion-electron pair correlation functions as well as the electron-electron susceptibilities. The latter are still quantum-mechanical, and cannot be simply connected to electron-electron pair correlations.

B. Quantum Hypernetted Chain Approximation

To make further progress, one needs a way of solving the QOZ relations for a liquid metal. We sketch the derivation here, for more details we refer to reference [15] and to the original work of Chihara [16,17]. As a first step, we use a quantum version of the Percus trick [18] to relate the *homogeneous* two-body pair-correlation functions to the one-body *inhomogeneous* density around a single classical particle fixed at the origin. For the ion-electron pair-correlation function we fix an ion at the origin to find:

$$g_{Ie}(\mathbf{0}, \mathbf{r}) = \frac{\rho_e(\mathbf{r}|I)}{\rho_e^0}, \quad (5)$$

where $\rho_e(\mathbf{r}|I)$ is the (interacting) valence electron density [19]. A similar relationship can be found for the ion-ion pair-correlation function, but this trick cannot be used for the electron-electron pair-correlation function, since one cannot “fix” an electron at one position. The next step is to solve for the interacting one-body electron-density. To do this, one can use the Kohn-Sham trick [3], namely that there exists a single-particle external potential $v^{\text{eff}}(\mathbf{r})$ which will induce in a *non-interacting* system the same one-particle density $\rho(\mathbf{r})$ as is found in the full *interacting* system. This external effective potential, felt by the non-interacting electrons or non-interacting ions, follows from the Euler equations. If one further makes a functional Taylor expansion around the equilibrium homogeneous densities, then the following effective ion-ion and ion-electron potentials result:

$$v_{\alpha I}^{\text{eff}}(r) = v_{\alpha I}(r) - \frac{1}{\beta} \sum_{\gamma} \rho_{\gamma} \int C_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|) h_{\gamma I}(r) d\mathbf{r}' + \frac{1}{\beta} B_{\alpha I}(r), \quad (6)$$

where the $C_{\alpha\gamma}(r)$ are the homogeneous limits of the direct correlation functions defined in Eq. (3), and the Percus trick was used to rewrite $(\rho_{\gamma}(\mathbf{r}|v_{\gamma I}) - \rho_{\gamma}^0)$ in terms of the correlation functions $h_{\gamma I}(r) = g_{\gamma I}(r) - 1$. The remaining higher order terms are lumped into the so-called *bridge functions* $B_{\alpha\beta}(r)$, well known in the theory of liquids [20,14].

Again, we note that no such potential can be derived for the electron-electron correlations. With that caveat in mind, our formulation, derived from a DFT approach, is still in principle exact.

To make progress, however, some approximations must be made, in particular to treat the electron-electron correlations. We follow Chihara, who made a series of such approximations to derive the QHNC equations [10]. The most important one is:

1. *The valence electron correlations are treated in the jellium approximation.* I.e. the effect of the ion-ion and ion-electron correlations on the electron-electron correlations are ignored, and the electron-electron direct-correlation function is written as:

$$C_{ee}(k) = -\beta v_{ee}(k)[1 - G_{ee}^{jell}(k; \rho_e^0)], \quad (7)$$

where G_{ee} is the local field factor for the electron gas [21,22]. This has the great advantage that the QOZ relations (3) now reduce to only two coupled equations for the ion-ion and the ion-electron correlations. While this is the key approximation that makes the QOZ relations tractable, it is also the most important and uncontrolled approximation in the QHNC scheme. The fact that the effective pair potentials derived from a linear response scheme [13,21] are very sensitive to the exact form of the local field factor also testifies to the importance of the approximations in Eq. (7) to the physics of a liquid metal.

QHNC also uses an implicit separation of the valence electrons from the core electrons. This approximation is closely related to the jellium approximation discussed above, and is only good when the core and valence electron energy levels are well separated so that the ionic correlations don't have a significant effect on the core states; it is likely to break down near resonances.

The other approximations used in QHNC are much better understood, and are often encountered in either their electronic structure [21] or liquid state theory context [14]. In descending order of importance they are (For a more detailed discussion see ref. [15].):

2. *The local density approximation (LDA) is used for the one-centre ion-electron problem.* This approximation is well known and understood in electronic-structure theory [21]. Although in principle this approximation is similar to approximation 1 for $C_{ee}(Q)$, since the exchange and correlation energy of an inhomogeneous electron gas are approximated by the local energy density of jellium, there are a number of reasons to believe the LDA is rather accurate [5]. Various improvements to the LDA exist, but these are not thought to be very important for the simple metals we study.
3. The ion-electron bridge function $B_{Ie}(r)$ is set to 0, which is related to the hypernetted-chain approximation, well known in liquid state theory [14].
4. The ion-ion bridge function $B_{II}(r)$ is approximated by the bridge-function of a hard-sphere reference state. This is called the RHNC or MHNC approximation in liquid state theory [14,20], and is generally very accurate.
5. The bare ion-ion potential is taken to be purely Coulombic. Again, this is an approximation whose limitations are well understood [21].

In summary then, the QHNC approximation achieves the following very important simplification for the electronic problem: the original many-centre electronic problem has been reduced to an effective one-centre problem by replacing the direct effect of the ions with an effective external potential, given by Eq. (6), that depends self-consistently on the ion-ion correlations. This is depicted schematically in Fig. 1. The main advantages are that the ion-ion and ion-electron correlations emerge naturally and on the same footing and that the calculations are much more rapid than full *ab initio* simulations. By using DFT to derive the QHNC equations, their origin and meaning becomes more transparent. For details on the (non-trivial) numerical implementation of the QHNC we refer to refs. [15–17].

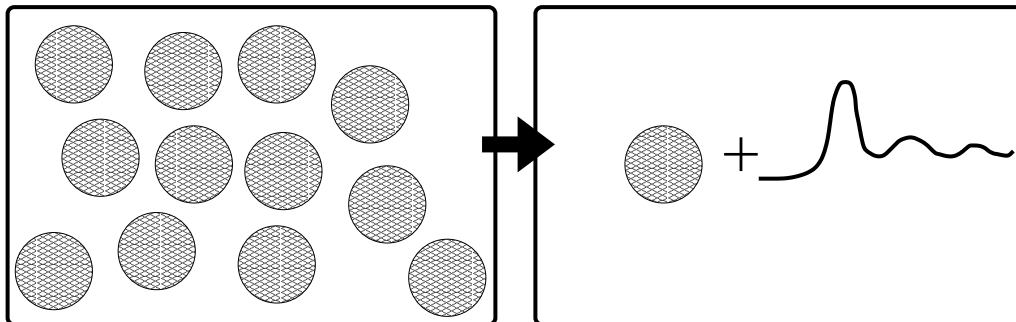


FIG. 1. Schematic picture of the QHNC approximation: The original many-centre problem is reduced to an effective one-centre problem.

C. Applications of the QHNC to ion-electron correlations

The ion-electron radial distribution function, defined as the conditional probability of finding a valence electron a distance r away, given that there is an ion at the origin, can be written as:

$$\rho_e^0 g_{Ie}(r) = n(r) + \rho_e^0 \int_V n(r - r') g_{II}(r') d\mathbf{r}', \quad (8)$$

where $n(r)$ is the so-called “pseudo-atom” density, which, when superimposed according the ion-ion radial-distribution function $g_{II}(r)$, gives the correct value of the total electron-density. The ion-electron radial distribution function and the related pseudo-atom density, calculated with the QHNC approach, are shown in Fig. 2 for a series of simple metals. At short distances the probability of finding an electron a distance r away is equal to the pseudo-atom density, but further away the effects of the other surrounding pseudo-atoms kick in. Note that the QHNC is an all-electron calculation; the oscillations near the core are correctly reproduced [19], in contrast to the traditional AIMD approaches, which rely on pseudopotentials. The ion-electron correlation functions calculated with the QHNC compare very well for the cases where AIMD simulations are available. However, it turns out that for most of the metals in our set a much simple linear response formalism also performs remarkably well [23]. The surprising accuracy of the linear response arises from a quantum interference effect between two length-scales: the Fermi wave-vector and the core-size of the ions, which makes the non-linear response terms much less important than one might naively expect [23]. The accuracy of the QHNC also benefits from this effect.

$g_{el}(r)$ and $n(r)$

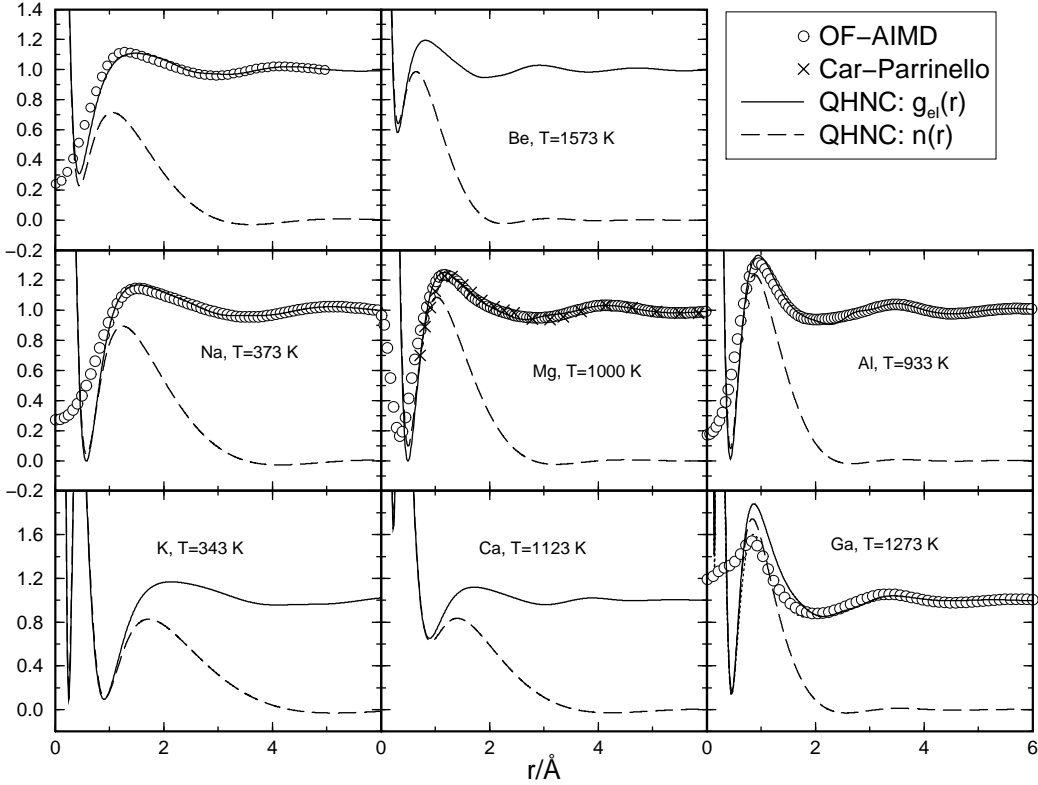


FIG. 2. The ion-electron radial distribution functions as obtained from the QHNC approximation (solid lines), OF-AIMD [34,35] (open circles) and Car-Parrinello AIMD [36] (crosses). The dashed lines represent the pseudo-atom density $n(r)/\rho_e^0$.

The only metal in our set where the QHNC has difficulty is Ga. We found earlier [15] that an ad-hoc change in the local field factor $G_{ee}(q)$ seems to improve matters. We also found that the d-electrons are close to a resonance. These two points indicate that approximation 1, discussed in the previous section, begins to break down for Ga.

III. APPLYING TWO-COMPONENT DFT TO INHOMOGENEOUS FLUIDS

In this section we explore the possibilities of studying inhomogeneous metals within a two-component DFT formulation. The advantage of treating metals directly as an electron-ion mixture in this way is that we bypass the need for effective (density dependent) ion-ion potentials. Modern classical DFT methods use input from the homogeneous liquid state [8,9,24,25]; the QHNC is ideally suited to provide such input for a two-component DFT.

One of the simplest approximations for the DFT of an inhomogeneous system, first proposed by Ramakrishnan and Yussouf (RY) [26,27], corresponds to truncating at second order a functional Taylor expansion of the excess free-energy around the homogeneous phase:

$$\Delta F^{ex}[\rho_I, \rho_e] = - \sum_{\alpha} \sum_{\beta} \int d\mathbf{r} \int d\mathbf{r}' \Delta \rho_{\alpha}(\mathbf{r}) C_{\alpha\beta}(\rho_{\alpha}^0, \rho_{\beta}^0; |\mathbf{r} - \mathbf{r}'|) \Delta \rho_{\beta}(\mathbf{r}'), \quad (9)$$

where $\Delta F^{ex} = F^{ex}[\{\rho_{\alpha}(\mathbf{r})\}] - F_0^{ex}(\{\rho_{\alpha}^0\})$, and the direct correlation functions $C_{\alpha\beta}(\rho_{\alpha}^0, \rho_{\beta}^0; |\mathbf{r} - \mathbf{r}'|)$ are those of the homogeneous liquid phase. For metals, the QHNC provides $C_{II}(r)$ and $C_{Ie}(r)$, while $C_{ee}(r)$ is fixed by the jellium approximation. Together, these correlation functions completely determine the excess free-energy of Eq.(9).

To obtain the total free-energy, one then adds the ideal contributions of the electrons and the ions. For the ions, this ideal free energy functional has the form:

$$\beta F_I^{id}[\rho_I] = \int d\mathbf{r} \rho_I(\mathbf{r}) \{ \ln [\rho_I(\mathbf{r}) \Lambda^3] - 1 \}, \quad (10)$$

but for the electrons the exact form is not known, and various approximations must be made. To preserve the advantages of the current DFT approach, one needs a kinetic energy functional. A number of forms have been proposed; some are remarkably accurate, see e.g. [7] and references therein. These kinetic energy functionals also vary in the ease with which they can be implemented in a full two-component DFT calculation [28].

Classical DFT has frequently been applied to the freezing transition and the fluid-solid interface of simple fluids [9]. The two-component DFT described above provides a basis upon which to build similar applications for metallic systems.

As a first application, we attempted to use the two-component RY formalism described above to calculate the freezing transition of Al. A very similar approach was already implemented by one of us [29] to study the freezing transition of H. However there a simpler semi-empirical prescription was used for $C_{Ie}(r)$. Since H does not have a core radius, the cancellation of higher order response terms found for simple metals [23] does not hold. This implies that the correlation functions and also the freezing transition of H should be more difficult to treat accurately than would be the case for simple metals. Other properties of liquid H , such as the metal-insulator transition [30] are also much harder to treat. Partially for these reasons, we would initially expect that the simple metals are actually better systems on which to test rudimentary DFT's.

The one-body densities of the solid phase are parameterized by sums over the reciprocal lattice vectors (r.l.v.) $\{\mathbf{G}\}$:

$$\rho_\alpha(\mathbf{r}) = \rho_\alpha^0 \sum_{\{\mathbf{G}\}} \xi_\alpha^{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}]. \quad (11)$$

For the ions a further, well established, simplification is to take the real-space density $\rho_I(\mathbf{r})$ as a sum of Gaussians, centred on the lattice sites, which implies $\xi_I^{\mathbf{G}} = \exp[-G^2/4\zeta]$. With this density parameterization and approximation, the full free-energy functional for the difference between the solid and the liquid state free energy, taken from Eqs. 1, 9 and 10, reduces to:

$$\begin{aligned} \frac{\beta \Delta F}{N_I} = & \left(\frac{3}{2} \ln \left[\frac{\zeta d^2}{\pi} \right] - \frac{3}{2} - \ln 2 \right) + \Delta F_e^{id}[\rho_e] - \frac{1}{2} \sum_{\{\mathbf{G}\}} '(\xi_I^{\mathbf{G}})^2 \rho_I^0 \hat{c}_{II}(|\mathbf{G}|) - \\ & \frac{1}{2} \sum_{\{\mathbf{G}\}} '(\xi_e^{\mathbf{G}})^2 \rho_e^0 \hat{c}_{ee}(|\mathbf{G}|) - \sum_{\{\mathbf{G}\}} ' \xi_I^{\mathbf{G}} \xi_e^{\mathbf{G}} \rho_e^0 \hat{c}_{Ie}(|\mathbf{G}|). \end{aligned} \quad (12)$$

Here the $\hat{c}_{\alpha\beta}(|\mathbf{G}|)$ are the Fourier transforms of the direct correlation functions for the liquid state, and the primes mean that the term $\mathbf{G} = 0$ should be omitted in the sum. The first term between brackets is the ideal free-energy of the ions (10), written out in terms of the Gaussian parameter ζ .

This free-energy can then be minimized through the variational principle (2) to solve for the free-energy difference between a given solid crystal structure and the fluid phase. However, when we attempted this for Al, with the direct correlation functions given by the QHNC, we found that the free energy of the solid did not have a stable minimum. This is a common problem encountered when applying a DFT to the freezing transition (see e.g. ref [31]): If the full direct correlation functions are used, then it is very hard to stabilize solid phase. If instead one uses the DFT for a hard-sphere reference system, adding the attractive interactions as a perturbation, very good agreement with experiment and simulation is recovered. Examples include phase diagram [24] and the fluid-solid interface of the LJ fluid [32], and a one-component treatment of the freezing of Al [33], based on an effective pair potential. This suggests that a successful 2-component DFT treatment of the freezing transition also needs to pass via this route. Unfortunately this quickly reduces to a theory similar to the one-component DFT, which means introducing the effective pair potentials we are trying to avoid in the first place.

Another application of the two-component DFT formalism is to examine the fluid-solid interface of Al, for which Besson and Madden [11] have recently completed extensive OF-AIMD simulations. They found non-trivial behaviour, with the ion-ion density profiles decaying from an ordered structure to a smooth liquid structure across several atomic layers. Similarly, they found that the valence electron density also showed oscillations which decayed into the bulk liquid phase. In principle, a two-component DFT would be ideally suited to study this problem, since the ionic and electronic density profiles come out on equal footing. Unfortunately, the difficulties encountered when trying to treat the freezing transition also make studying this problem very difficult. Instead, we tackle a simpler problem: Given the ionic density profile, can we use our DFT to calculate the electron density profile?

If the ionic density profiles are given, which fixes the $\xi_I^{\mathbf{G}}$, then the electronic $\xi_e^{\mathbf{G}}$ which satisfy the variational principle (2) follow from Eq. (12):

$$\xi_e^{\mathbf{G}} = -\frac{\xi_f^{\mathbf{G}} \hat{c}_{Ie}(\mathbf{G})}{(\beta/\chi_{ee}^0(\mathbf{G})) + \hat{c}_{ee}(\mathbf{G})}. \quad (13)$$

where we have made an additional approximation, also made in [29], namely that the ideal electron contribution $\Delta F_e^{id}[\rho_e]$ is expanded to second order in $\xi_e^{\mathbf{G}}$ (linear response). This is consistent with the spirit of the RY DFT approach, and greatly simplifies the minimization of the electronic degrees of freedom, since they are now linearly coupled to the ionic ones. Note that taking the lowest order approximation to the ion-electron direct correlation function, $C_{Ie}(r) \approx -\beta v_{Ie}(r)$ in Eq. (13) would be equivalent to a standard linear response calculation. Since we use the full $C_{Ie}(r)$, non-linear response terms are included, although one would need to use the full kinetic energy functional to be completely consistent with the RY DFT approach of Eq. (12). The results of using Eq.(13) are shown in Fig. 3 as a function of the distance z along the interface. (See ref. [11] for details of parameters). The QHNC results are in fact less accurate than a simpler linear-response approximation which replaces $\hat{c}_{Ie}(G)$, with an empty-core Ashcroft pseudopotential [13,21]. At first this may seem surprising, but a careful look at the inset of Fig. 3 shows that the difference results from the fact that $\hat{c}_{Ie}(G)$ is considerably smaller at $G \approx 1.8$, where the strongest ionic scattering occurs. This difference stems in part from the fact that the true pseudopotential in Al is known to be highly non-local [21] because of the p character of the bonds, suggesting that a local formulation, such as the simple linear response DFT we employed, will not work well together with the QHNC calculation which makes no local pseudopotential assumptions. Non-linear response effects are also expected to be more important at the highly inhomogeneous fluid-fluid interface. In contrast to the QHNC, the pseudo-potential contains an empirically adjustable parameter which effectively includes non-local and non-linear effects. To achieve accurate results with a DFT based on the QHNC, one needs to treat the two approaches at comparable levels of approximation. As is often encountered in condensed-matter physics, mixing different levels of approximation does not work very well. Two ways of improving this would be **(1)** to use QHNC with the improved local pseudopotentials used in the OFMD [11] or **(2)** to use a more sophisticated DFT approach. Although far from complete or completely satisfactory, this first, and rather primitive, example of a two-component DFT used for a liquid-solid interface suggests that our DFT approach could in principle be fruitfully used to study fluid-solid interfaces in simple metals.

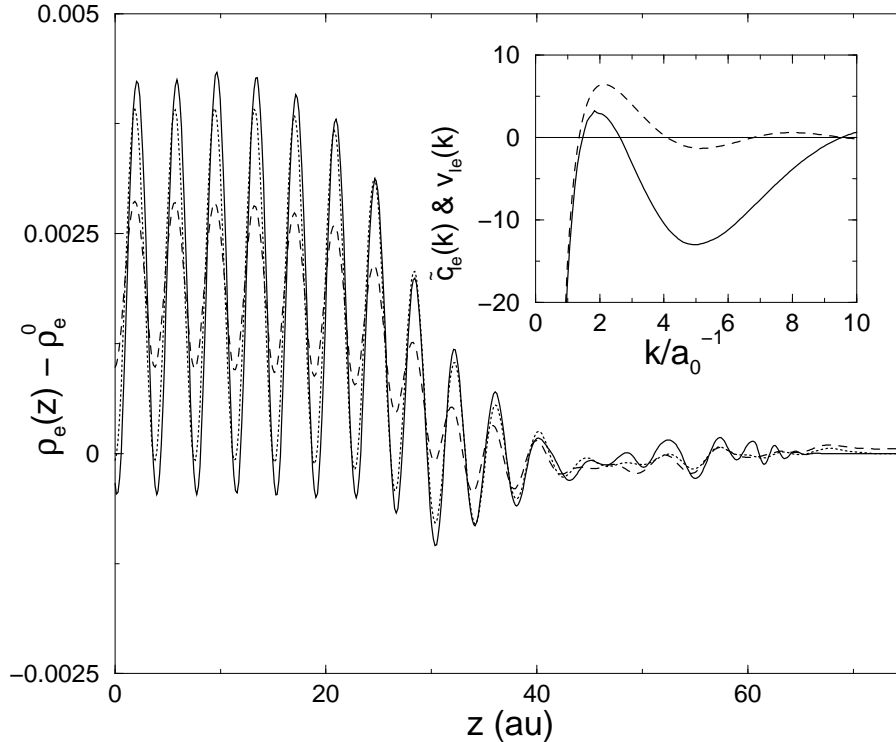


FIG. 3. Electron density profiles from the OF-AIMD simulations [11] (solid lines), compared to the QHNC-DFT results (dashed lines) given by Eq. (13), and linear response theory (dotted lines) with an empty-core pseudopotential with $R_c = 1.153a_0$. Inset, comparison of $\hat{c}_{Ie}(k)$ (solid line) and the pseudopotential $v_{Ie}(k)$ (dashed line), both in Hartrees.

IV. CONCLUSIONS

In conclusion, we have shown how DFT provides a unified formalism from which to derive the QOZ equations, and the related QHNC approach, first pioneered by Chihara. The QHNC reduces the many-centre electronic problem to an effective one-centre one. This dramatically reduces the computational time needed to calculate ion-electron and ion-ion correlation functions. It also has the advantage that no explicit use of effective pair potentials or pseudo-potentials is needed. The most important approximation in the QHNC approach is to treat the electron-electron correlations as those of jellium. It is not yet clear under which conditions this approximation begins to break down. With this caveat in mind, the other approximations entering the QHNC are reasonably well understood. We used the QHNC to calculate the ion-electron radial distribution functions for a number of simple metals, finding very good agreement with ab-initio molecular dynamics calculations where these are available.

We have also discussed an exploratory application of the simple RY DFT approach to liquid metals as two-component electron-ion mixtures. We found that describing the freezing transition suffers from a similar problem to that found for classical simple fluids: the solid phase does not develop a stable minimum if the full direct correlation functions are used as input. This is rather disappointing. Slightly more (partial) success was found when we attempted to use the DFT to describe the inhomogeneous electron density at a liquid-solid Al interface. Although this result was only a partial application of the DFT, since the ionic density profile came from the simulations, it does suggest that developing a full fledged DFT could be very fruitful. Finally, it is clear that our rudimentary DFT approach is not yet accurate enough, and could be improved in a number of ways. We are attempting to generalize more sophisticated DFT schemes like the MDWA [25] or GELA [8] to the two-component ion-electron problem. We are also studying the effect of using different local field factors and different kinetic energy functionals.

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